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Inelastic collisions between excited sodium atoms and molecules.

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INELASTIC COLLISIONS BETWEEN EXCITED SODIUM ATOMS AND MOLECULES

by

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ABSTRACT

$^2P_{1/2} \longleftrightarrow {}^2P_{3/2}$ mixing in sodium vapour, induced by inelastic collisions with the diatomic molecules H_2, HD, D_2 and N_2, was studied using techniques of sensitized fluorescence. The mixtures of sodium vapour with the various molecular gases were irradiated with one component of the appropriate resonance doublet. The fluorescence which contained both components of the doublet, was monitored at right angles to the direction of excitation. The measurement of the relative intensities of the fluorescent components yielded the total inelastic cross sections for ^2P mixing, $Q_{12}(^2P_{1/2} \longrightarrow {}^2P_{3/2})$ and $Q_{21}(^2P_{1/2} \longleftarrow {}^2P_{3/2})$. The sodium vapour in the fluorescent cell was maintained at a pressure of 5×10^{-7} mm Hg to avoid radiation trapping, and the molecular gas pressures ranged from 0 - 1 mm Hg. The quenching cross sections which were required to account for the quenching of sodium resonance radiations by H_2, HD, D_2 and N_2 had been obtained by Kibble, Copley and Krause (1967b)

The following values of the mixing cross sections were obtained. For Na-H_2: $Q_{12} = 80.3$ Å^2, $Q_{21} = 42.1$ Å^2. For Na-HD: $Q_{12} = 84.1$ Å^2, $Q_{21} = 43.9$ Å^2. For Na-D_2: $Q_{12} = 98.3$ Å^2, $Q_{21} = 51.8$ Å^2. For Na-N_2: $Q_{12} = 143.7$ Å^2, $Q_{21} = 75.9$ Å^2. These cross sections

were only slightly larger than the corresponding sodium-inert gas cross sections. The ratios Q_{12}/Q_{21} are in agreement with the value predicted from the principle of detailed balancing.

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I. INTRODUCTION

When a cell containing pure sodium vapour at low pressure or a sodium vapour-molecular gas mixture is illuminated with one component of the sodium resonance doublet, both fine structure components will appear in the fluorescence. The component having the same wavelength as is used for excitation is known as resonance fluorescence and the other component whose presence results from the collisional excitation transfer is called sensitized fluorescence. The mixing induced in the ^2P state of an excited sodium atom by a collision with a diatomic molecule M proceeds according to the equation,

$$Na(3^2P_{1/2}) + M + \Delta E \rightleftharpoons Na(3^2P_{3/2}) + M \qquad (1)$$

where ΔE, the energy difference between the fine structure components (17.2 cm^{-1}), is supplied or carried away by the various degrees of freedom of the colliding partners. Molecules are known to be very efficient in causing collisional deactivation of the ^2P sodium atoms to the ground state (Pringsheim, 1949). This quenching reaction proceeds according to the equation,

$$Na(3^2P_J) + M \rightleftharpoons N(3^2S_{1/2}) + M^* \qquad (2)$$

where M^* is a molecule which, having participated in an inelastic collision, has become modified in its content of translational,

vibrational and rotational energy. The quenching cross section for the molecule M must be known for each resonance level to account for such occurrences.

The study of inelastic collisions between heavy, low velocity particles has been a subject of much interest in recent years. The investigation of such phenomena has gained impetus from the current interest in energy transfer processes in the ionosphere, stellar atmospheres and especially the gas laser where the population inversion is accomplished by collision induced transitions between excited states.

The early studies of sensitized fluorescence in alkali metals were summarized by Krause (1966). McGillis and Krause (1967,1968) described the first sensitized fluorescence experiments with mixtures of alkali vapours and molecular gases. The most recent work with sodium-molecule mixtures was carried out by Casey (1967), who determined the quenching and mixing cross sections for collisions between sodium and N_2, H_2 and CO. However, because of the small separation between the fine structure levels, efficient resolution of the NaD lines without serious loss of intensity was difficult. Thus he found it necessary to illuminate the fluorescing vapour with both lines simultaneously and to monitor the degree of mixing as a function of inert gas pressure by scanning the fluorescent spectrum with a spectrometer and recording the D_2/D_1 intensity ratio in the fluorescent light. This method assumes that the D_2/D_1 intensity ratio in the

exciting light remains constant throughout each experiment and that increasing the pressure of the molecular gas influences equally the absorption profiles of both D lines.

The many theoretical attempts to interpret the mixing process induced by collisions with inert gas atoms were discussed by Pitre (1967). It might be expected that since molecules have more degrees of freedom than atoms and usually possess permanent multipole moments, they would produce mixing with greater efficiencies than those predicted by the current atom-atom collision theories but any explicit theoretical treatment of ^2P mixing produced by molecular collisions has not yet been attempted. The bulk of the relevant atom-molecule work has centered on the quenching process. These theories and their contributions to the understanding of the mixing problem were discussed by McGillis (1967).

The present research concerns itself with the determination of the cross sections for mixing between the $^2P_{1/2}$ and $^2P_{3/2}$ resonance levels in sodium induced by collisions with non-polar diatomic molecules, in order to provide a firm experimental basis for a better understanding of inelastic atom-molecule collision processes.

II. RATE EQUATIONS FOR THE SENSITIZED FLUORESCENCE AND QUENCHING PROCESSES

The processes that take place when a mixture of sodium vapour and molecular gas is irradiated continuously with the D_2 component of the sodium resonance doublet are shown schematically in Fig. 1. The solid arrows indicate transitions giving rise to sensitized fluorescence and the broken arrows represent collisional deactivation of the 3^2P sodium atom to the ground state, which manifests itself by the quenching of the resonance radiation.

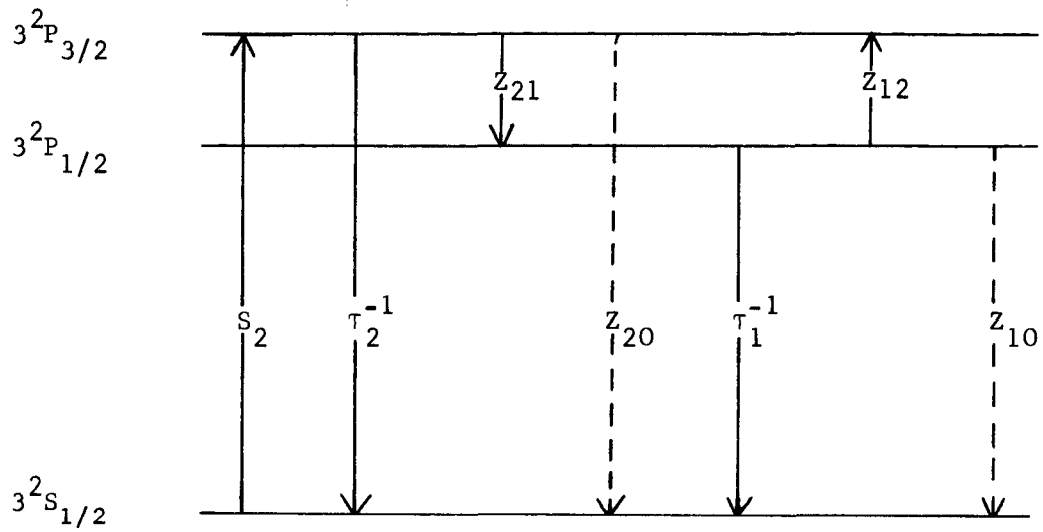

Fig. 1. Energy levels involved in sensitized fluorescence and in the quenching of sodium resonance radiation induced in collisions with molecules.

The various interactions between a sodium atom and a diatomic molecule M may be represented by the following equations:

$$Na(3^2S_{1/2}) + h\nu_2 \xrightarrow{S_2} Na(3^2P_{3/2}) , \quad (3)$$

$$Na(3^2P_{3/2}) + M \xrightarrow{Z_{21}} Na(3^2P_{1/2}) + M^* , \quad (4)$$

$$Na(3^2P_{1/2}) + M \xrightarrow{Z_{12}} Na(3^2P_{3/2}) + M^* , \quad (5)$$

$$Na(3^2P_{3/2}) + M \xrightarrow{Z_{20}} Na(3^2S_{1/2}) + M^* , \quad (6)$$

$$Na(3^2P_{1/2}) + M \xrightarrow{Z_{10}} Na(3^2S_{1/2}) + M^* , \quad (7)$$

$$Na(3^2P_{3/2}) \xrightarrow{(\tau_2)^{-1}} Na(3^2S_{1/2}) + h\nu_2 , \quad (8)$$

$$Na(3^2P_{1/2}) \xrightarrow{(\tau_1)^{-1}} Na(3^2S_{1/2}) + h\nu_1 , \quad (9)$$

where S_2 is the number of sodium atoms excited per second from the $3^2S_{1/2}$ state to the $3^2P_{3/2}$ state, τ_1 and τ_2 are the mean lifetimes of the $^2P_{1/2}$ and $^2P_{3/2}$ states ($\tau_1=\tau_2=\tau = 1.63 \times 10^{-8}$ sec. (Kibble, Copley and Krause, 1967a)) and Z_{21}, Z_{12}, Z_{20} and Z_{10} are the collision numbers for the processes designated in Fig. 1, defined as the numbers of collisions per excited sodium atom per second, leading to the appropriate process of excitation transfer. M is a ground-state diatomic molecule and M^* a molecule which, having participated in an inelastic collision, has become modified in its content of translational, vibrational and rotational energy.

Collisional mixing of the ^2P states due to Na-Na collisions

has been neglected since the ratio of sensitized to resonance fluorescent intensities due to such collisions is of the order of 10^{-6} at the vapour pressure used in the experiment (5×10^{-7} mm Hg) and does not contribute significantly to the observed sensitized fluorescence (Pitre and Krause, 1968).

Assuming that the vapour-gas mixture exists in a state of dynamic equilibrium involving only continuous optical excitation of the $Na(3^2P_{3/2})$ state by means of D_2 radiation, spontaneous decay, and the various binary collisional processes, Eqs. (3) - (9) may be combined to give the following rate equations:

$$\frac{dn_2}{dt} = 0 = Z_{12}N_1 - \frac{n_2}{\tau} - Z_{21}n_2 - Z_{20}n_2 \quad , \tag{10}$$

$$\frac{dn_1}{dt} = 0 = Z_{21}N_2 - \frac{n_1}{\tau} - Z_{12}n_1 - Z_{10}n_1 \quad . \tag{11}$$

N refers to the density of atoms in the state being optically excited, n refers to the density of atoms in the other ^2P state and τ is the average lifetime of the ^2P states.

Dividing (10) and (11) by N_1 and N_2, respectively, yields

$$Z_{12} = (\frac{1}{\tau} + Z_{21} + Z_{20})\,\eta_2 \quad , \tag{12}$$

and

$$Z_{21} = (\frac{1}{\tau} + Z_{12} + Z_{10})\,\eta_1 \quad , \tag{13}$$

where

$$\eta_1 = \frac{I(D_1)}{I(D_2)} = \frac{n_1}{N_2} \quad , \tag{14}$$

$$\eta_2 = \frac{I(D_2)}{I(D_1)} = \frac{n_2}{N_1} \quad . \tag{15}$$

I refers to the fluorescent intensity and the wavelengths in the denominators are, in each case, the same as those used in the exciting light.

Solving (12) and (13) for Z_{12} and Z_{21} gives,

$$Z_{12} = \frac{\tau^{-1}(\eta_2 + \eta_1\eta_2) + Z_{10}\eta_1\eta_2 + Z_{20}\eta_2}{1 - \eta_1\eta_2} \quad , \tag{16}$$

and

$$Z_{21} = \frac{\tau^{-1}(\eta_1 + \eta_1\eta_2) + Z_{20}\eta_1\eta_2 + Z_{10}\eta_1}{1 - \eta_1\eta_2} \quad . \tag{17}$$

Because of the small energy difference between the $3^2P_{1/2}$ and $3^2P_{3/2}$ states of sodium, equal quenching cross sections for the two states are expected. Hence, taking $Z_{20} = Z_{10}$ (Kibble, Copley and Krause, 1967b), equations (16) and (17) become respectively:

$$Z_{12} = \frac{(\eta_2 + \eta_1\eta_2)}{1 - \eta_1\eta_2} [\tau^{-1} + Z_{10}] \quad , \tag{18}$$

and

$$Z_{21} = \frac{(\eta_1 + \eta_1\eta_2)}{1 - \eta_1\eta_2} [\tau^{-1} + Z_{10}] \quad . \tag{19}$$

The collision numbers Z are functions of temperature:

$$Z(T) = N \int q(v)\, v\, f_T(v)\, dv \quad , \tag{20}$$

where N is the density of ground state atoms, $q(v)$ is the differential cross section, v is the velocity of relative motion and $f_T(v)$ is the Maxwell-Boltzmann probability that at a temperature T colliding partners will have a relative velocity between v and v + dv.

By analogy with the gas kinetic cross section an effective total cross section Q may be defined by,

$$Z_{12} = N Q_{12} v_r \quad , \tag{21}$$

and

$$Z_{21} = N Q_{21} v_r \quad , \tag{22}$$

where v_r is the mean relative velocity

$$v_r = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \tag{23}$$

and where k is Boltzmann's constant and μ is the reduced mass of the colliding atoms.

According to the principle of detailed balancing the ratio of the cross sections should be,

$$\frac{Q_{12}}{Q_{21}} = \frac{g_2}{g_1} \exp\left(\frac{-\Delta E}{kT} \right) , \tag{24}$$

where $g_1 = 2$ and $g_2 = 4$ are the statistical weights of the $^2P_{1/2}$ and $^2P_{3/2}$ states, respectively, and the Boltzmann factor, $\exp\left(\frac{-\Delta E}{kT} \right)$, is the probability that in a collision the kinetic energy

of relative motion will be greater than ΔE where ΔE is the energy difference between the ^2P fine structure components.

It has been assumed in the above treatment that there is no imprisonment of radiation. If resonance radiation were trapped, the effective lifetime of the ^2P levels would no longer be equal to their mean lifetime and this would result in spurious values of the cross sections.

III. DESCRIPTION OF THE APPARATUS

A. General Description

The arrangement of the apparatus is shown in Fig. 2. Sodium resonance radiation emitted from a sodium spectral lamp was passed through a rectangular slit, was collimated and was resolved into the component D lines by interference filters. The resulting monochromatic beam was focused into the fluorescence cell containing sodium vapour at a controlled pressure. The fluorescent light emitted from the vapour normally to the incident beam was collimated, resolved into its two D components by interference filters and brought to a focus on the S_{20} photocathode of a liquid air cooled photomultiplier, whose output pulses were amplified, passed through a discriminator and registered with a scaler. Motor-driven filter holders in the incident and fluorescent beams, controlled by an electromechanical sequencing system integrated with the pulse counting train, allowed for an automatically programmed sequence of operations (Pitre, 1965). The complete apparatus was enclosed in a light-tight box in order to eliminate stray light.

B. The Spectral Lamp

Studies of sensitized fluorescence in low density alkali vapours require a stable lamp which should emit intense D-lines of

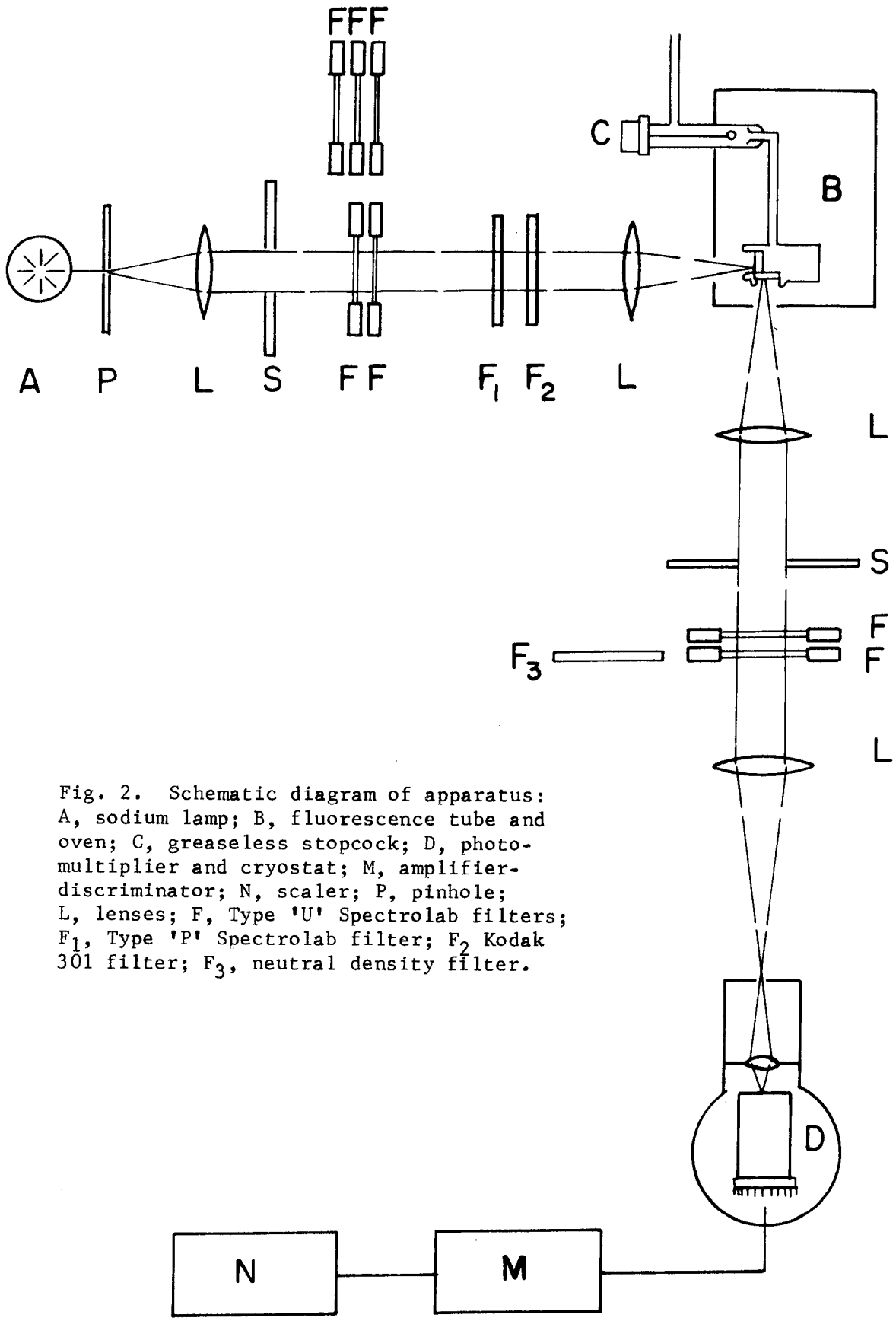

Fig. 2. Schematic diagram of apparatus: A, sodium lamp; B, fluorescence tube and oven; C, greaseless stopcock; D, photomultiplier and cryostat; M, amplifier-discriminator; N, scaler; P, pinhole; L, lenses; F, Type 'U' Spectrolab filters; F_1, Type 'P' Spectrolab filter; F_2 Kodak 301 filter; F_3, neutral density filter.

small half-width and negligible self reversal. The present lamp fulfils the above requirements to a high degree. The resonance radiation is emitted from a discharge tube containing a small quantity of sodium and about 1 mm Hg of argon, which is placed in a coil forming part of the tank-circuit in a rf oscillator.

The oscillator, whose circuit is shown in Fig. 3, was operated in class C in a push-pull configuration and employed 4-65A tetrodes whose typical power requirements were 150 ma. at 800 v.

The tuned circuit and the lamp excitation coils, both 2 cm. long and 2 cm. in diameter, consisted of 5 turns of 12 gauge tinned copper wire. The excitation coil was silvered because the rapid melting of the tin and subsequent oxidation of the copper resulted in a large resistive power loss in the coil. The small dimensions of the excitation coil necessitated the employment of heaters at both ends of the discharge tube. For maximum intensity, the end containing the sodium and hence controlling the vapour pressure was maintained at 210°C while the other end was maintained at about 230°C.

Each heater consisted of 4 ohms of resistance wire wound around an aluminum tube coated with Sauereisen for electrical insulation. The tube was inserted in a block of transite which acted as a thermal insulator. The end of the discharge tube was inserted in the end of the aluminum tube. A Veco 41A2 thermistor served as the sensing element for temperature controller whose circuit is

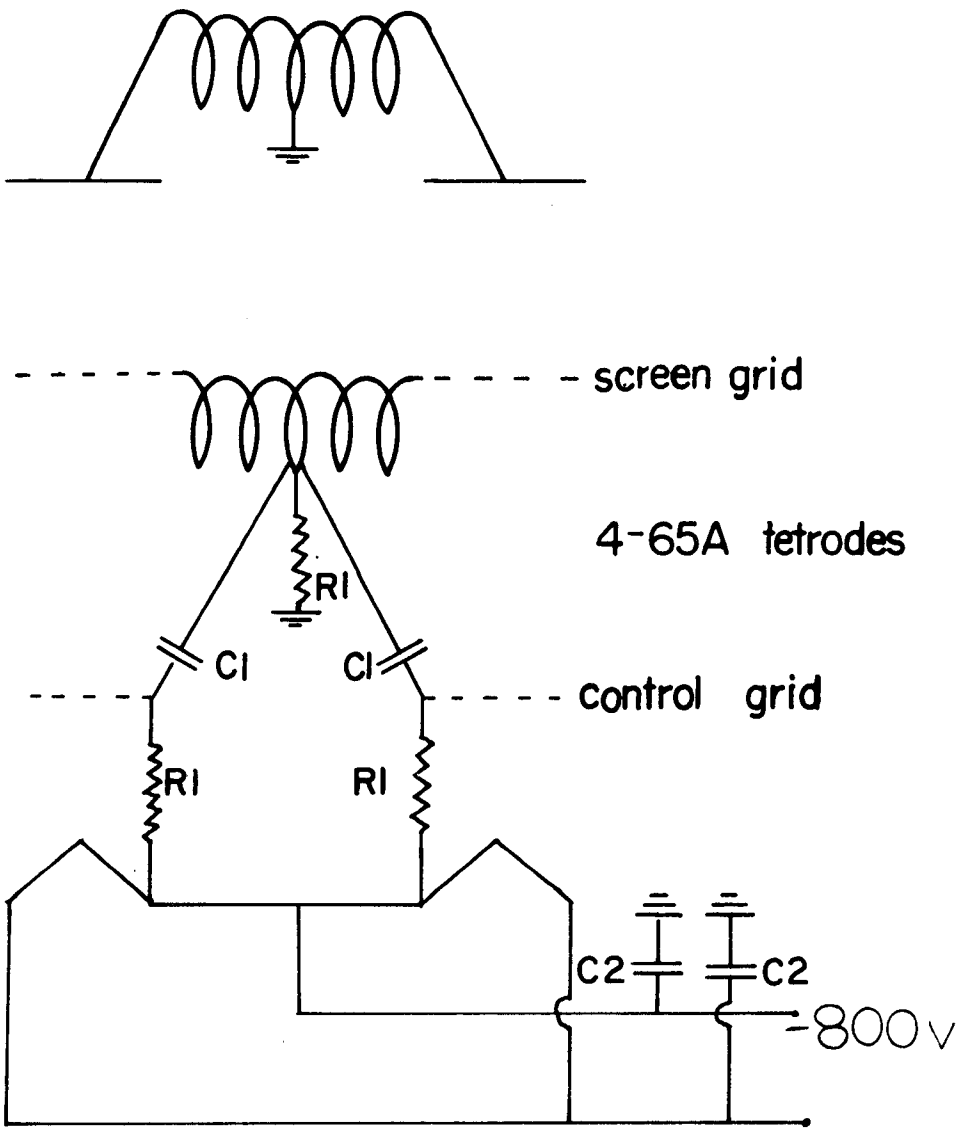

Fig. 3. The R.F. Lamp Circuit: C1, 150 pf; C2, 0.1μf; R1, 68K ohms.

shown in Fig. 4.

The main problem with sodium RF lamps is caused by the rapid discolouration and crystallization of pyrex glass and, to a lesser extent, of Corning 1720 'alkali resistant' glass by the corrosive action of hot sodium. This difficulty was overcome by using the inner discharge tube of a Philips spectral lamp which showed no signs of discolouration or deterioration after one week of continuous operation. Great care had to be taken in starting and stopping of the discharge as the tube tended to crack under thermal stress.

The lamp was operated at 165 Mc/s. following the suggestion of Bell, Bloom and Lynch (1961) that excitation by frequencies higher than 30 Mc/s. should produce an increase in lamp intensity since reduction in skin depth would reduce the thickness of the ring discharge and result in less self absorption. This lamp was 3 times more efficient in exciting resonance fluorescence than new Commercial Osram lamps but showed no definite increase over lamps operated at 40 Mc/s. The lamp was very stable and, during the experiment, the intensity of the resonance fluorescence was found to vary within less than $\pm$ 2 per cent over a 12 hour period.

C. Interference Filters

Spectrolab Type 'U' interference filters were used for the separation of the sodium resonance doublet. These filters

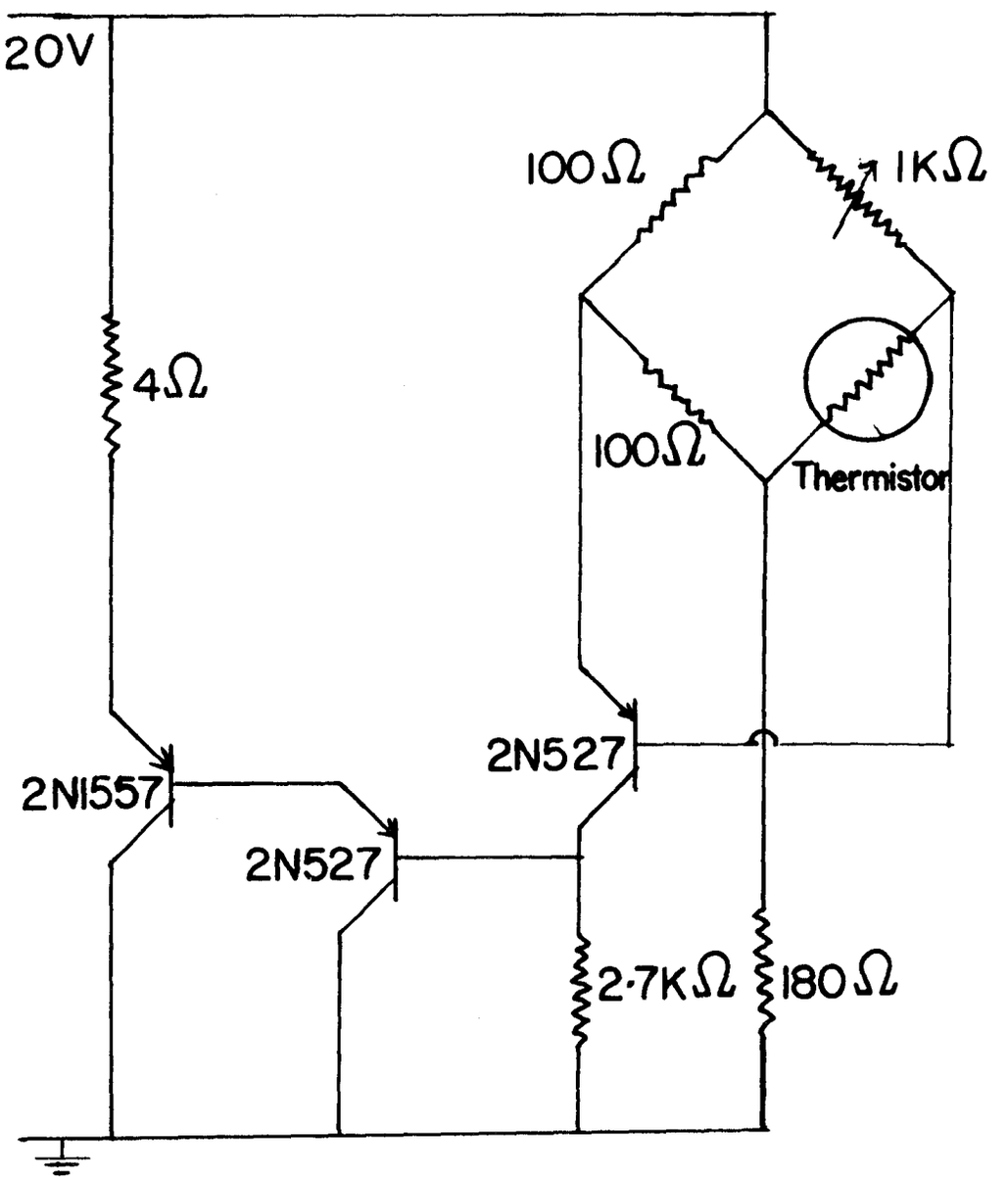

Fig. 4. The Lamp Heater Control Circuit.

typically transmitted about 60 per cent of the wanted resonance line and about 1 per cent of the unwanted component. Two D_1 filters in series producing a spectral purity of about 5 parts in 10^5 or three D_2 filters in series producing a spectral purity of about 5 parts in 10^6 were used in the exciting beam. The exciting light was also passed through a Spectrolab Type 'P' interference filter with a 60 Å transmission band width centred at the NaD lines and through a Kodak '301' short wave pass filter, whose purpose was to remove all other alkali resonance radiation which would cause fluorescence in traces of alkali impurities that might be present in the sodium. Precise knowledge of the transmissions of the filters in the incident beam to the NaD lines was not required since this information is not needed for the calculation of cross sections. The NaD lines in the fluorescent spectrum were separated by two Type 'U' D_1 filters with an overall transmission of 31 per cent to the D_1 line and 5×10^{-3} per cent to the D_2 line.

A series of slits and stops ensured that, in both the exciting and fluorescent beams, the light passing through the interference filters was strictly parallel as it must be for optimal resolution. The stops also confined the light beams to the central regions of the filters since their edges appeared to reject less efficiently the unwanted spectral components than their central portions. The filters were mounted in holders which allowed them to be precisely oriented with respect to each other and to the light

beam, and to be rotated about the light axis. These holders were mounted on motor-driven slides operated by an electromechanical sequencing system capable of automatic operation (Pitre, 1965).

D. The Fluorescence Cell

The design of the fluorescence cell, shown in Fig. 5, minimizes both unwanted absorption of the incident beam and trapping of resonance radiation. Reflections were suppressed by coating the cell and the vacuum connections with Aquadag, a colloidal dispersion of graphite. The exciting beam was focused in the corner formed by the entrance and exit windows. To minimize imprisonment of radiation, the image of the slit, which was 2.7 mm wide, was positioned about 0.5 mm from the side window of the cell. With this arrangement, the fluorescent light had to pass through only a very thin layer of unexcited atoms before escaping from the cell and yet the reflected light in the cell amounted to only 0.5 per cent of the resonance fluorescent intensity.

E. The Ovens

The oven containing the fluorescent cell consisted of a double-walled copper box, thermally insulated from the outside by glass wool. The exciting and fluorescent beams passed through pyrex glass windows set in annular teflon plugs. The heater, a 56 ohm coil wound non-inductively on a ceramic tube was mounted in one corner

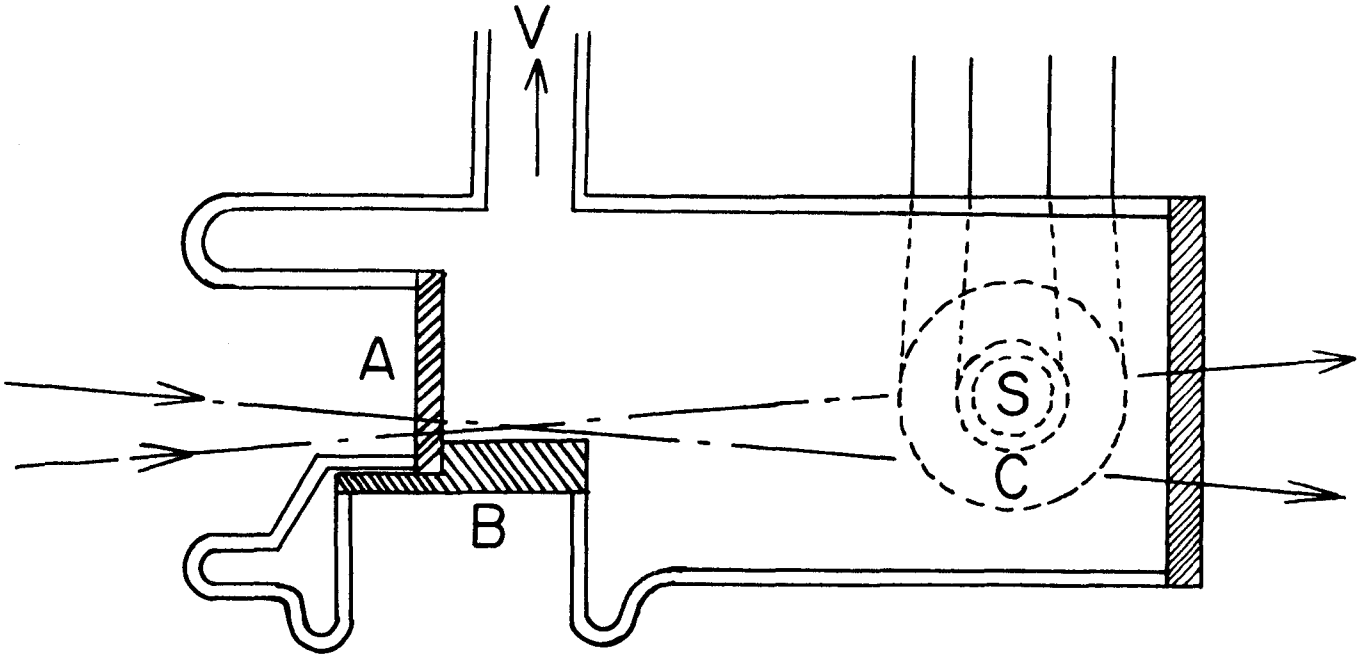

Fig. 5. The Fluorescence Cell: A, entrance window; B, side window; S, side arm; C, copper tubing from the ultrathermostat which controls the side arm temperature; V, connection to vacuum system.

behind a copper shield coated with Aquadag and heating took place by convection. The A.C. current for the heater was controlled by a powerstat and a saturable core reactor. Control of the D.C. current for the latter was provided by a transistorized D.C. amplifier employing a suitably placed Veco 41A2 thermistor as a sensing element. The circuit of this heater control unit was described by Pitre (1965).

The temperature of the side-arm of the fluorescence cell, which contained the liquid sodium, was controlled by circulating from a Jena Ultrathermostat, Dow Corning No. 200 fluid of 10 centistoke viscosity, through a closely fitting 3/16 inch copper coil surrounding the side arm. With this arrangement the main oven temperature could be stabilized within $\pm$ 0.1°C over a range extending from 25°C to 200°C and the side arm temperature could be maintained within $\pm$ 0.05°C over a range extending from 100°C to 200°C. All temperatures were measured by means of copper-constantan thermocouples and a Leeds and Northrup model 8662 potentiometer.

F. Vacuum and Gas Handling System

The glass system was evacuated by an Edwards E02 diffusion pump, equipped with an Edwards H5L2A baffle valve and a low resistance liquid air trap, backed by an ES 35 rotary pump. The diffusion pump was protected from cooling water failures by an FSM-1 Flowtrol unit. The lowest reproducible pressure obtained, using Dow Corning 704

Silicone fluid in the diffusion pump, was about 5×10^{-8} mm Hg. Vacuum measurements were carried out with a GIC-110 A CVC ionization gauge (10^{-3}-10^{-8} mm Hg) and a 3294 B LKB Autovac gauge (10^{-2}-10^{-3} mm Hg). Molecular gas pressures were measured approximately with the Autovac gauge and then, more accurately, with a liquid air-trapped CVC type GM-100 A McLeod gauge, (10-10^{-3} mm Hg).

The molecular gases were first dried by slow passage through a liquid air trap and then gettered by bubbling through 1.5 cm. of liquid cesium. The gases were next gettered for a two-day period in a storage bottle whose walls were coated with cesium, and then the storage bottle was immersed in liquid air for 3 days, to remove the cesium vapour from the gas. Before being admitted to the fluorescence cell, the gas was again dried by slow passage through a liquid air trap the purpose of which was to prevent water vapour, driven out of the glass surfaces, from entering the fluorescence cell.

G. The Detection and Recording System

An I.T.T. type FW-130 X, 16 dynode, end-on photomultiplier, cooled in a liquid air cryostat was used to detect the fluorescent light. The 1.3 kv operating voltage was supplied by a 412-B Fluke regulated power supply and was distributed at about 80 volts per stage by means of a resistive divider chain. The Sb-K-Na-Cs photocathode which had a S20 spectral response and a quantum efficiency of about 7.5 per cent for the NaD lines, was 0.1 inch in diameter.

Pulses from the photomultiplier were passed through a PW 4270 Philips amplifier-discriminator and were recorded on a PW 4230 scaler. The scaler readings were registered by means of a Victor printer used in conjunction with a PW 4200 printer control. The photomultiplier was connected directly to the amplifier-discriminator; no preamplification of the pulses was necessary. The dark noise of the photomultiplier was 30 counts/min. (equivalent to a D.C. dark current of 2×10^{-14} amp) and remained constant for many months. The tube had a gain of 3×10^{5} for the 60 per cent of the pulses which were above the discriminator threshold level, and an effective quantum efficiency* of 4.5 per cent.

The dead time of the counting system, which depends on the height and decay time of the photomultiplier pulses and on the setting of the discriminator, was obtained using the following formula applicable to a non-paralyzable counter:

$$a = \frac{A}{(1 - A\tau_o)} \quad , \tag{25}$$

where a is the true count rate, A is the observed count rate and τ_o is the dead time. The true count rate 'a' was found by inserting an

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* The effective quantum efficiency is the product of the photocathode efficiency (7.5 per cent at 5890 Å for an S20 surface) and a factor arising from the use of pulse discriminating techniques.

electrometer between the anode of the photomultiplier and ground, and measuring the photomultiplier current, g. The relation,

$$g = ka \quad , \tag{26}$$

where k is a constant, assumes only that the photomultiplier output is linear with input intensity. Combining equations (25) and (26) gives,

$$\frac{1}{A} = \frac{k}{g} + \tau_o \quad . \tag{27}$$

A plot of $\frac{1}{A}$ versus $\frac{1}{g}$ yielded the dead time τ_o which was found to be 1.26 ± 0.1 μ sec. and gave rise to corrections, never exceeding 1.5 per cent, to the observed counting rate.

The following modifications in the amplifier PW 4270 were made, which decreased the dead time by about 14 per cent. In addition, the input capacitance which included the output capacitance from the photomultiplier and the stray capacitances of the leads to the amplifier, was reduced from 67 pf to 40 pf.

The input transistor OC47 was replaced by a Fairchild 2N3640 PNP high speed logic switch which has a very small open base capacitance. The input to the amplifier was placed directly through the side of the amplifier and was only about one cm. from the base of the input transistor. The output of the photomultiplier was only 2 cm. away from the input to the amplifier. The above mentioned changes had negligible effect on the gain and the pulse shaping characteristics of the amplifier.

IV. EXPERIMENTAL PROCEDURE

At the start of each experiment, the system was baked at a pressure of 1×10^{-7} mm Hg. The temperature of the sodium in the side arm of the fluorescence cell, which controlled the vapour pressure, was 115°C and corresponded to a vapour pressure of 5×10^{-7} mm Hg. The higher temperature in the main part of the cell, 125°C, prevented condensation of the sodium on the windows. When a vacuum of 5×10^{-8} mm Hg was reached, the appropriate gas was admitted to the cell from a Pyrex bottle which had been previously connected to the system and which was opened under vacuum by a glass-enclosed magnetic breaker. Linde M.S.C. grade H_2 and N_2 (nominal purity 99.99 per cent), HD (99 per cent) supplied by Stohler Isotope Chemicals, and Matheson Reagent grade D_2 (99.99 per cent), were used in the experiment. The gas was dried by slow passage through a liquid air trap and was gettered by bubbling through 1.5 cm. of cesium. The gettering was continued for two further days in a storage bottle whose walls were coated with cesium and then the storage bottle was immersed for three days in liquid air to remove the cesium vapour from the gas. Before being admitted to the fluorescence cell, the gas was again dried by slow passage through a liquid air trap.

The transmissions of the filter sets were measured in

situ and were remeasured several times during the experiments. The transmission of a Type 'U' Spectrolab filter to the appropriate NaD component depends on the polarization of the incident light (Dobrowolski, 1959). Thus the D_2 component in the fluorescent light could not be directly isolated by means of the appropriate filter because of its partial linear polarization which amounted to about 5 per cent in pure sodium vapour and which decreased rapidly with increasing gas pressure. Instead, the intensity of the D_2 component in the fluorescent light was obtained by subtracting the intensity of the D_1 component, measured with the D_1 filters in the fluorescent light beam, from the total fluorescent light intensity.

For each gas pressure, the electromechanical sequencing system (Pitre, 1965) controlling the motor-driven slides which held the interference filters in the incident and fluorescent beams, was programmed for eight alternating measurements of η_1 and η_2 values. Each η value was determined from two alternating one minute photon count accumulations carried out with and without the interference filters in the fluorescent light beam. The arithmetic mean of these results was accepted as the η_1 and η_2 value, respectively, corresponding to the particular gas pressure.

The dark noise of the photomultiplier, which amounted to 30 counts/minute, resulted, in the case of the sensitized fluorescence measurements, in a signal-to-noise ratio ranging from 100 to 1000.

For the much more intense resonance fluorescence, the dark noise was negligible, but corrections to the measured fluorescent intensities were made for reflected light in the cell which contributed 0.5 per cent to the observed signal.

The D_2 light in the incident beam was 83 per cent linearly polarized with the axis of polarization at an angle of 65 degrees to the incident beam direction. This polarization was due to the optical activity of the mica in the interference filters. the polarization of the D_2 resonance line in the fluorescent beam was 5.5 per cent for zero molecular gas pressure and would decrease rapidly with increasing gas pressure (Mitchell and Zemansky, 1961). A simple calculation (Feofilov, 1961) showed that under these conditions the effects arising from the anisotropy of the D_2 radiation on the calculation of the η values were negligible.

V. RESULTS AND DISCUSSION

A. Experimental Results

The experimental values of the fluorescent intensity ratios, η_1 and η_2, obtained in mixtures of sodium vapour with nitrogen, hydrogen, deuterium hydride and deuterium, are shown in Tables 1 - 4 respectively. Each Table represents values obtained in at least two experimental runs with increasing and decreasing molecular gas pressures. Figures 6 and 7 are the graphical representations of Tables 1 and 4 and of Tables 2 and 3, respectively, and show plots of the η-values against pressures of nitrogen and deuterium and of hydrogen and deuterium hydride, respectively.

Experimental values of η_1 and η_2 were used in a computer programme to obtain the collision numbers Z_{12} and Z_{21} from Equations (18) and (19) and hence, from Equations (21) and (22), the corresponding values for the cross sections Q_{12} and Q_{21} which were then averaged and yielded the final cross section for the particular sodium-molecular gas collisional process. The collision number Z_{10} for $3^2P_{1/2} \longrightarrow 3^2S_{1/2}$ quenching, needed in Equations (18) and (19), was calculated from the quenching cross sections obtained by Kibble, Copley and Krause (1967b). The differences between the individual Q_{12} or Q_{21} values, before averaging, were small as may

TABLE 1

Fluorescent Intensity Ratios for Sodium-Nitrogen Collisions

N_2 Pressure (mm Hg)	η_1	η_2
.135	.0301	.0596
.150	.0339	.0650
.227	.0490	.0980
.265	.0560	.1110
.280	.0585	.1169
.325	.0669	.1360
.358	.0719	.1455
.451	.0870	.1780
.461	.0883	.1810
.475	.0910	.1907
.572	.1042	.2180
.615	.1089	.2330
.625	.1115	.2340
.636	.1130	.2370
.684	.1190	.2540
.700	.1210	.2560
.768	.1290	.2750
.860	.1390	.3030
.905	.1440	.3120

TABLE 4

Fluorescent Intensity Ratios for Sodium-Deuterium Collisions

D_2 Pressure (mm Hg)	η_1	η_2
.084	.0258	.0500
.114	.0346	.0682
.132	.0390	.0760
.143	.0418	.0820
.184	.0525	.1059
.212	.0600	.1190
.201	.0564	.1125
.233	.0648	.1307
.270	.0724	.1467
.317	.0828	.1694
.335	.0867	.1810
.340	.0890	.1830
.365	.0932	.1945
.435	.1070	.2280
.442	.1077	.2265
.460	.1130	.2390
.532	.1250	.2700
.593	.1360	.2940
.670	.1490	.3250
.695	.1530	.3340
.711	.1550	.3400
.825	.1710	.3800
.840	.1720	.3800
.980	.1900	.4310

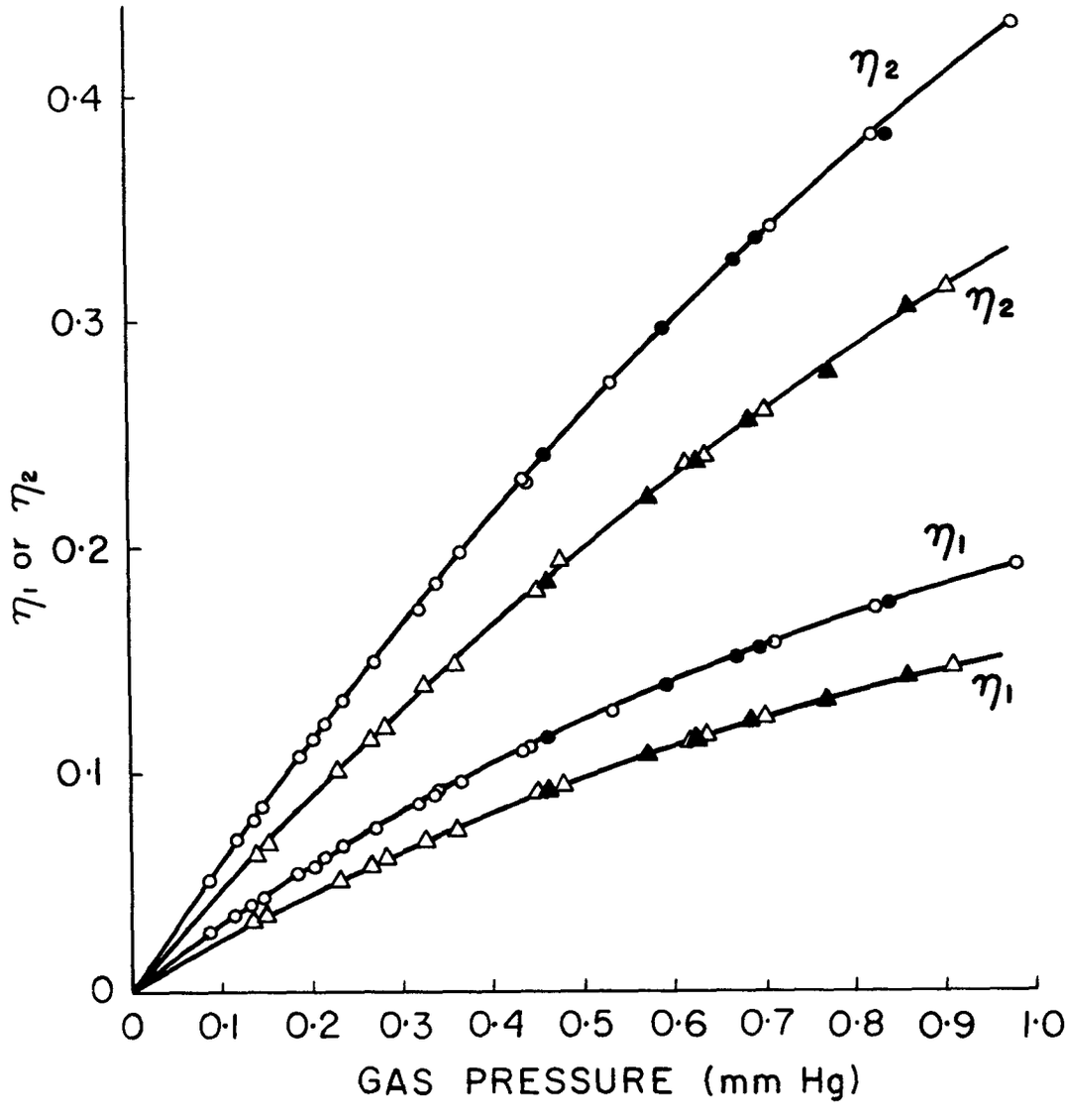

Fig. 6. Plots of the fluorescent intensity ratios η_1 and η_2 against D_2 and N_2 pressures. o and • represent values obtained for increasing and decreasing D_2 pressures, respectively; △ and ▲ represent values obtained for increasing and decreasing N_2 pressures, respectively.

TABLE 2

Fluorescent Intensity Ratios for Sodium-Hydrogen Collisions

H_2 Pressure (mm Hg)	η_1	η_2
.104	.0346	.0682
.115	.0368	.0728
.145	.0460	.0922
.172	.0528	.1051
.210	.0639	.1300
.213	.0645	.1300
.260	.0762	.1554
.267	.0786	.1600
.335	.0938	.1950
.350	.0975	.2000
.420	.1100	.2350
.471	.1206	.2600
.610	.1444	.3180
.680	.1531	.3420
.802	.1740	.3890
.800	.1723	.3861
.918	.1870	.4280
.999	.1941	.4580

TABLE 3

Fluorescent Intensity Ratios for Sodium-Deuterium Hydride Collisions

HD Pressure (mm Hg)	η_1	η_2
.145	.0408	.0809
.242	.0643	.1305
.271	.0709	.1447
.370	.0914	.1910
.300	.0770	.1580
.450	.1061	.2253
.564	.1258	.2720
.605	.1330	.2880
.677	.1430	.3140
.740	.1515	.3378
.850	.1670	.3750
.999	.1841	.4240

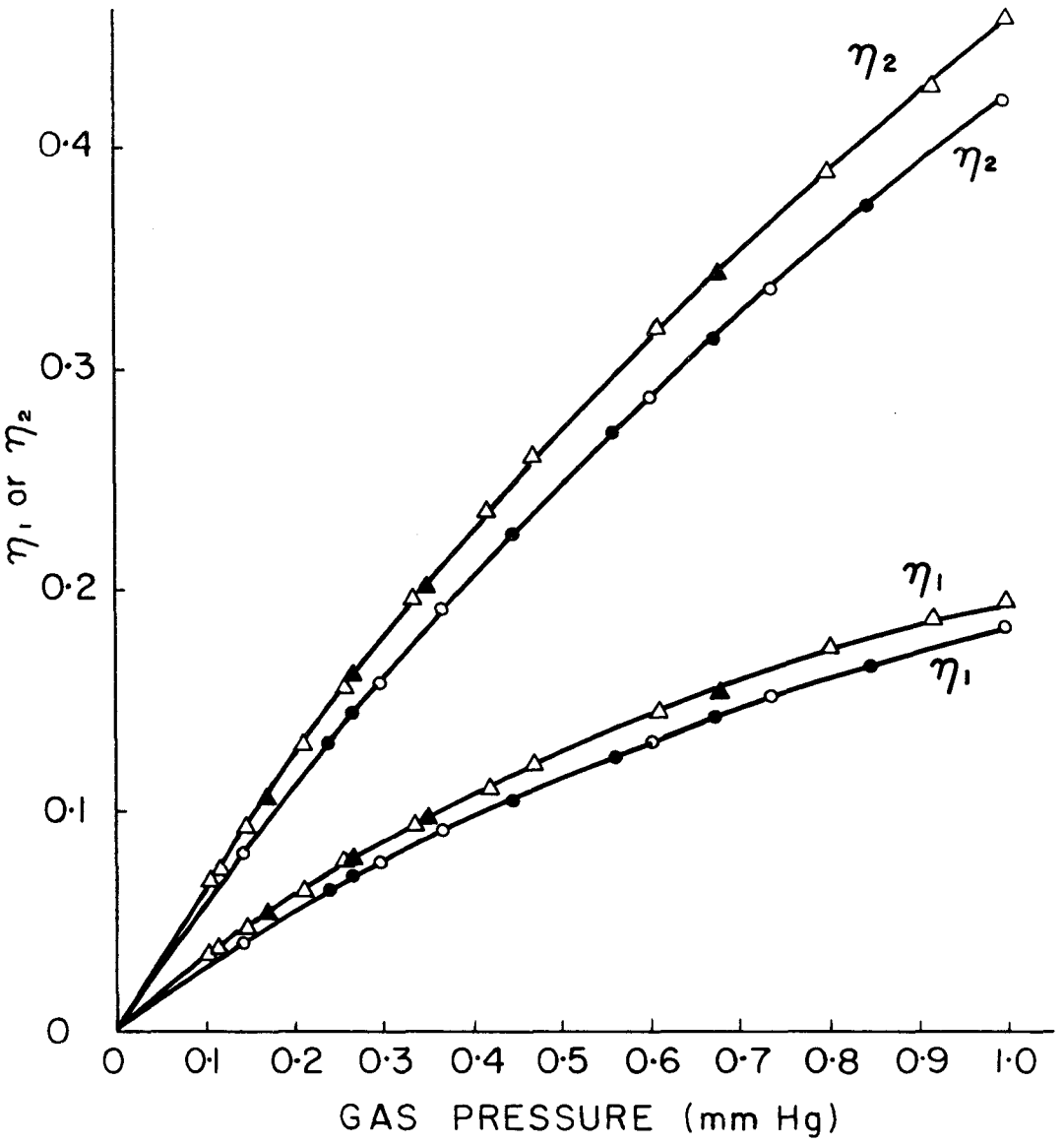

Fig. 7. Plots of the fluorescent intensity ratios η_1 and η_2 against H_2 and HD pressures. △ and ▲ represent values obtained for increasing and decreasing H_2 pressures, respectively; o and • represent values obtained for increasing and decreasing HD pressures, respectively.

be seen in the plots of the collision numbers Z_{12} and Z_{21} against pressures of nitrogen, hydrogen, deuterium hydride and deuterium, which appear in Figures 8, 9, 10 and 11, respectively. In these Figures, the crosses represent the collision numbers Z_{12} and Z_{21} as calculated from Equations (18) and (19), assuming the quenching collision number Z_{10} being equal to zero, and the circles represent the collision numbers Z_{12} and Z_{21} corrected for the quenching effect. The circles lie on two straight lines whose slopes are proportional to the cross sections Q_{12} and Q_{21}.

Table 5 shows the collision cross sections Q_{12} and Q_{21}, together with the only other experimental values quoted by Casey (1967).

B. Accuracy of the Results

The statistical uncertainty in the mixing cross sections Q_{12} and Q_{21} was smaller than 1 per cent for all the mixtures. The systematic errors introduced by the temperature measurements, McLeod gauge readings and filter transmissions were estimated to be about 3 per cent each and the mean lifetime of the sodium resonance states and the quenching cross sections for these states were also considered to be accurate within 3 per cent. When all of these error sources are taken into account, the mixing cross sections are thought to be correct within 7 per cent.

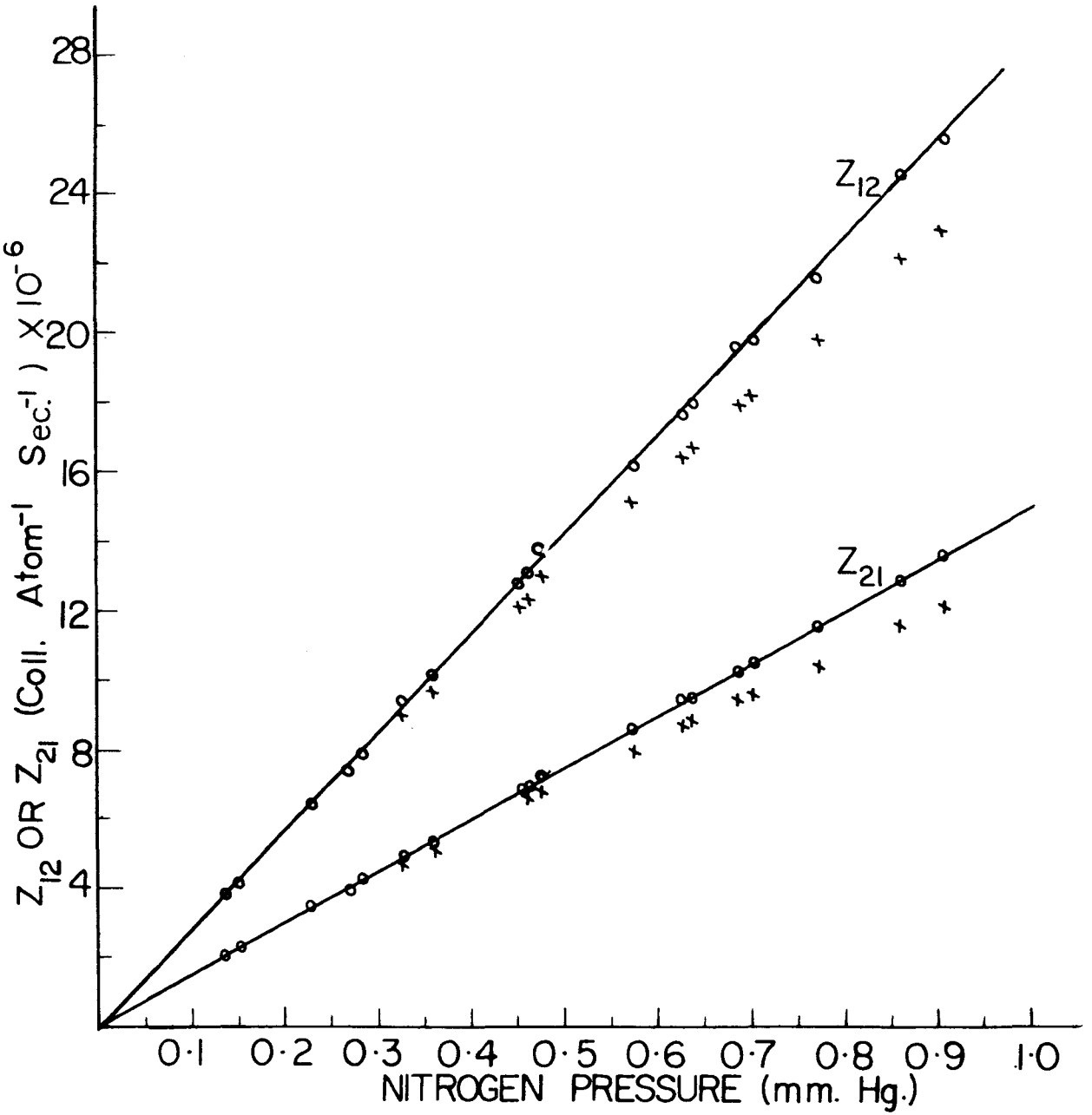

Fig. 8. Plots of the collision numbers Z_{12} and Z_{21} against N_2 pressure.

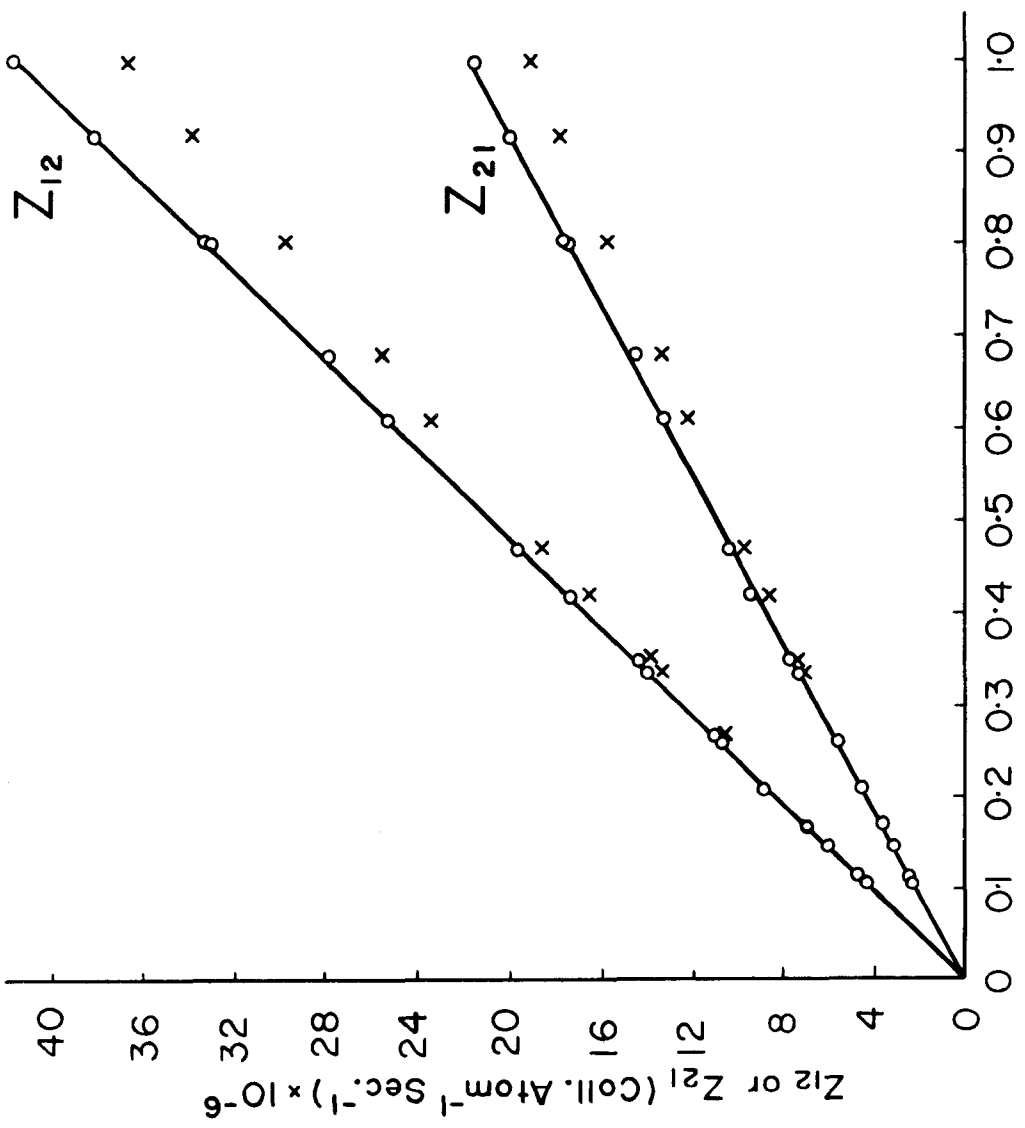

Fig. 9. Plots of the collision numbers Z_{12} and Z_{21} against H_2 pressure.

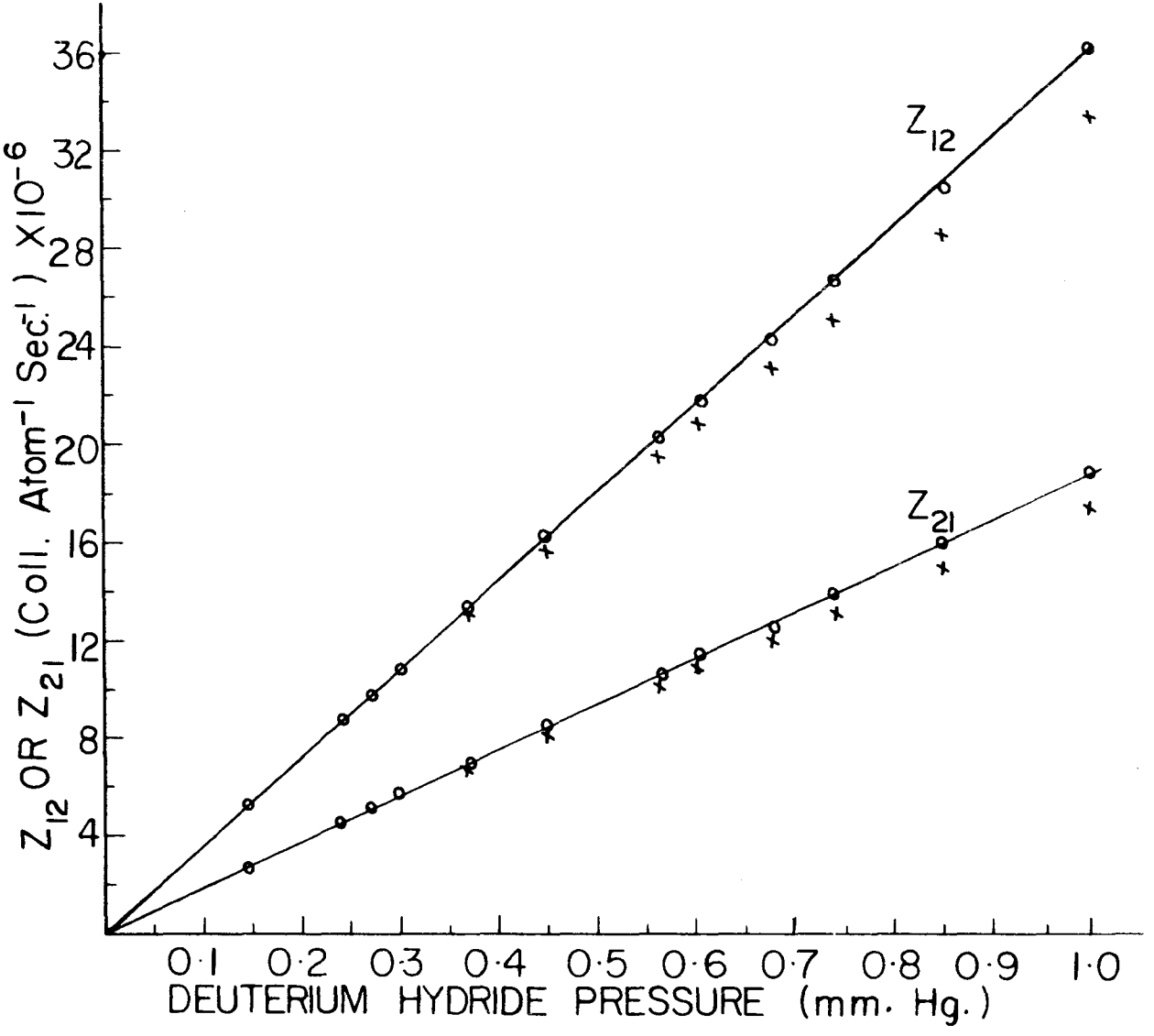

Fig. 10. Plots of the collision numbers Z_{12} and Z_{21} against HD pressure.

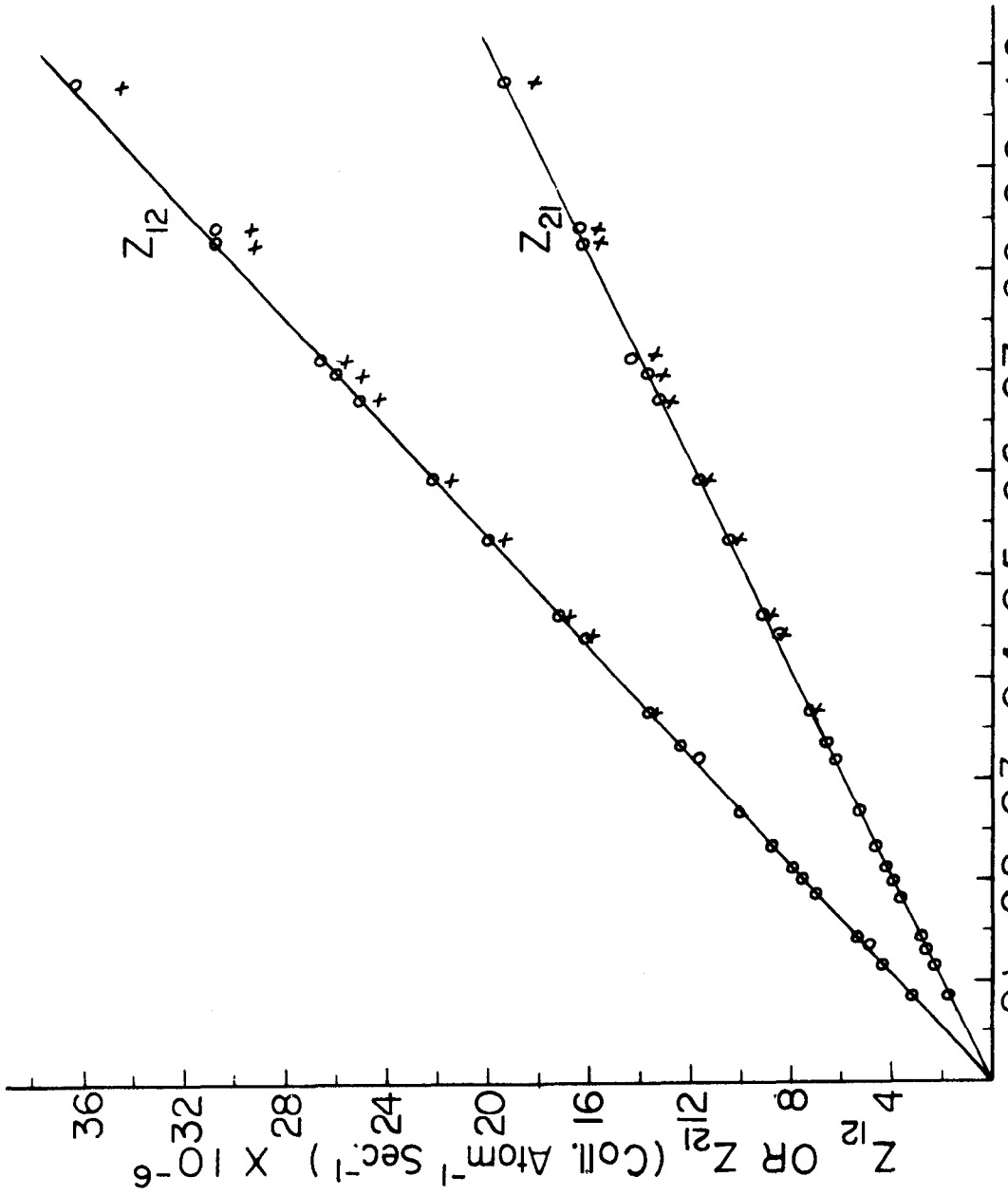

Fig. 11. Plots of the collision numbers Z_{12} and Z_{21} against D_2 pressure.

TABLE 5

Cross Sections For $3^2P_{1/2}$—$3^2P_{3/2}$ Mixing Induced By Sodium–Molecule Collisions

Collision Partners	Designation Q_{12} OR Q_{21}	This Investigation			Casey (1967)
		Q_{12} OR Q_{21} ($Å^2$)	Q_{12}/Q_{21}	$2e^{-\Delta E/kT}$	Q_{12} OR Q_{21} ($Å^2$)
Na–N_2	Q_{12}	143·7	1·90	1·88	
	Q_{21}	75·9			22
Na–D_2	Q_{12}	98·3	1·90	1·88	
	Q_{21}	51·8			
Na–HD	Q_{12}	84·1	1·92	1·88	
	Q_{21}	43·9			
Na–H_2	Q_{12}	80·3	1·91	1·88	
	Q_{21}	42·1			10

C. The ^2P Mixing Cross Sections

The sodium-molecule ^2P mixing cross sections Q_{12} and Q_{21} are of the same order of magnitude as the corresponding sodium-inert gas cross sections (Pitre and Krause, 1967). This seems to confirm the suggestion of McGillis and Krause (1968), who found a similar relationship for potassium-molecule collisions, that the interaction which causes spin-orbit decoupling in an excited alkali atom is not appreciably stronger for non-polar diatomic molecules than for inert gas atoms.

Table 5 shows that there is a small variation in the ^2P mixing cross sections for H_2, HD and D_2. It is expected that the interaction mechanism for ^2P mixing would be the same for these isotopic molecules since H_2, HD and D_2 have similar electronic structures. Hence, this small variation in the ^2P mixing cross sections may well be due to the difference between the masses of these isotopic molecules, which affects the vibrational and rotational energy of the molecules as well as the relative velocity of the colliding partners. There appears to be no correlation of the mixing cross sections with the molecular rotational levels and, indeed, none is to be expected because H_2, HD and D_2 have no rotational transitions in the range of the energy defect ΔE, between the sodium resonance levels. Fig. 12 shows the first few rotational levels for H_2, HD, D_2 and N_2 and the allowed rotational transitions. At the temperature

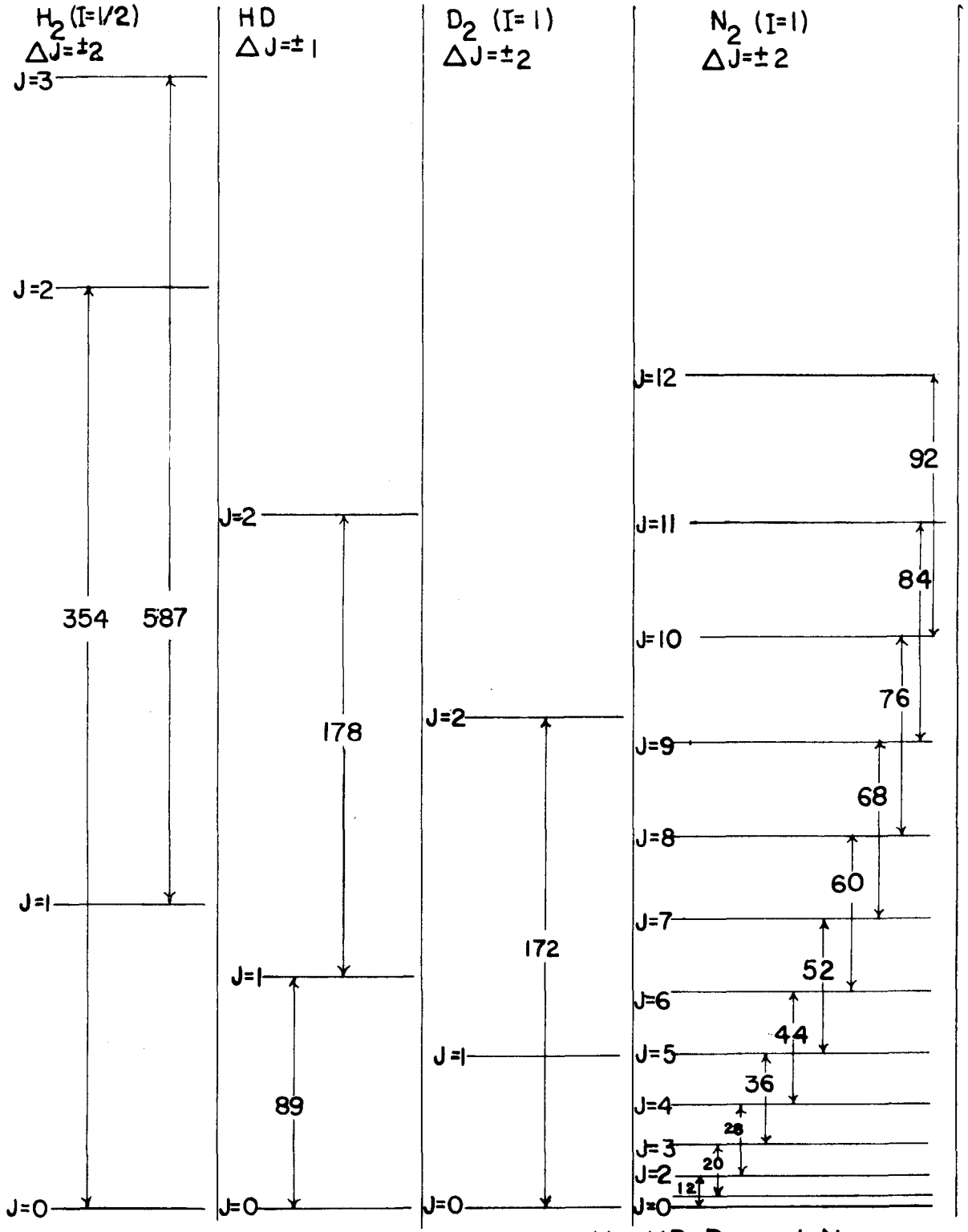

Fig. 12. Some Rotational Levels for H_2, HD, D_2 and N_2. Energy Differences are in $cm.^{-1}$.

of the experiment ($398^{o}K$), most of the H_2, HD and D_2 molecules are in the J=0, J=1 and J=2 rotational levels with the population peak centred at the J=1 level. If the mixing cross sections for H_2, HD and D_2 were to exhibit a correlation with the molecular rotational levels, the magnitude of the HD cross section should be largest followed by D_2 and then H_2 since ΔE for sodium is only 17 cm^{-1}. This was not observed to be the case.

The larger Na-N_2 cross section may be due to the fact that N_2 has many closely spaced rotational levels and the energy of some rotational transitions fall in the range of the energy defect between the sodium resonance levels (McGillis and Krause, 1967). An exact resonance with rotational transitions is probably not necessary because the energy defect in sodium is less than kT(274 cm^{-1}) and, with the available excess of translational kinetic energy, ^2P mixing would not depend exclusively on a concurrent rotational transition taking place in the participating molecule.

Table 6, shows the Q_{21} and Q_{12} mixing cross sections for collision of sodium with H_2, HD and D_2, together with the corresponding relative velocity of the colliding partners. The ^2P mixing cross section for the isotopic molecules H_2, HD and D_2 appear to increase in magnitude with decreasing relative velocity of the colliding partners. A similar effect has been observed by McGillis (1968) for the cesium-methane system.

TABLE 6

Cross Sections for Excitation Transfer in Na-Molecule Collision, together with the Corresponding Relative Velocity of the Colliding Partners

Collision Partners	$Q_{21}(\text{Å})^2$	$Q_{12}(\text{Å})^2$	v_r(cm/s)
Na-H_2	42.1 ± 2.7	80.3	2.08×10^5
Na-HD	43.9 ± 3.1	84.1	1.73×10^5
Na-D_2	51.8 ± 3.6	98.3	1.53×10^5

The relatively large disagreement of the Q_{21} results for N_2 and H_2 obtained in this experiment and those obtained by Casey (1967) may well be due to the large influence, which pressure broadening and shift of the D-lines in absorption, would exert on the ^2P excitation transfer measurements carried out with his experimental method. It should also be considered that a relatively large amount of scattered light is present in the Jarrell Ash scanning spectrometer used by Casey, as compared with the unwanted stray light transmitted through the interference filters used in this investigation.

Table 7, shows the cross sections Q_{12} and Q_{21} for $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ mixing in alkali metals, induced by collisions with diatomic

TABLE 7

Comparison of the Cross Sections for $^2P_{1/2} \rightleftharpoons {}^2P_{3/2}$ Mixing Induced by Alkali Atom-Molecule Collisions

Source	Collision Partners	$Q_{21}(\text{Å})^2$	$Q_{12}(\text{Å})^2$	$Q_{21}(\text{Å})^2$ with inert gases (Krause, 1966)
This Investigation	Na-H_2	42.1	80.3	43.6 ——— 55.9
	Na-HD	43.9	84.1	
	Na-D_2	51.8	98.3	
	Na-N_2	75.9	143.7	
McGillis and Krause (1968)	K-H_2	53.2	75.6	9.45 ——— 72.3
	K-HD	48.7	74.0	
	K-D_2	50.4	72.2	
	K-N_2	66.0	99.7	
McGillis and Krause (1967)	Cs-H_2	43.8	6.7	3.1×10^{-4} —— 27.4×10^{-4}
	Cs-HD	32.1	4.8	
	Cs-D_2	27.8	4.2	
	Cs-N_2	25.2	4.7	

molecules, obtained in this laboratory. This Table has a very interesting feature. The sodium-molecule and the potassium-molecule ^2P mixing cross sections are of the same order of magnitude as the sodium-inert gas and potassium-inert gas cross sections,

while the cesium-molecule mixing cross sections are five orders of magnitude larger than the cesium inert gas cross sections. Such a large disparity between the mixing efficiencies in cesium of molecules and inert gas atoms cannot be attributed to their different interaction potentials since no such vast difference in the mixing cross sections was observed in the sodium or potassium systems. The determining factor seems to be that the energy defect between the cesium ^2P states, which equals 554 cm^{-1}, falls within the energy range of the molecular rotational levels. In the case of sodium and potassium, such resonances with the molecular levels are much less important as in this case, the available thermal energies are more than sufficient to bridge the $^2P_{1/2} \rightleftharpoons {}^2P_{3/2}$ energy gaps. The study of ^2P mixing in cesium induced by collisions with ortho- and para-hydrogen which is now being carried out in this laboratory should clarify the role that molecular rotational levels play in the ^2P mixing process.

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VITA AUCTORIS

I was born on April 4th, 1944, in Glozan, Yugoslavia, and came to Canada with my family in 1953. I attended the Kingsville District High School and upon graduation in 1963 I enrolled at the University of Windsor with an Ontario Scholarship and an entrance scholarship; the latter I maintained until my graduation in Honours Physics in 1967. During my undergraduate years, I also received Bursaries and Scholarships from the Hydro-Electric Power Commission of Ontario and the Aluminum Company of Canada. I then entered the Faculty of Graduate Studies to proceed toward a Master of Science degree in Physics. I was aided in the past year by a National Research Council graduate Bursary.